



Kurose, T., Shirai, R., Vasiljevic, N., & Hayase, M. (2019). Miniature Fuel cell with Monolithically Fabricated Si Electrode -First prototype with Au-Pd-Pt multilayer catalyst-. In *18th International Conference on Micro and Nanotechnology for Power Generation and Energy Conversion Applications 4–7 December 2018, Daytona Beach, Florida, USA* (1 ed., Vol. 1407). [012008] (Journal of Physics: Conference Series; Vol. 1407). <https://doi.org/10.1088/1742-6596/1407/1/012008>

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To cite this article: T. Kurose *et al* 2019 *J. Phys.: Conf. Ser.* **1407** 012008

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Miniature Fuel cell with Monolithically Fabricated Si Electrode

-First prototype with Au-Pd-Pt multilayer catalyst-

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Abstract. Our first fuel cell prototype with a novel Au-Pd-Pt catalyst successfully demonstrated power generation. In order to reduce amount of platinum group metals and obtain high CO tolerance, electrochemical atomic layer depositions of Pd and Pt were applied on the porous Au. 5 ML Pd and sub-ML Pt deposition was attempted and amounts of Pd and Pt were electrochemically estimated to be 125 $\mu\text{g}/\text{cm}^2$ and 6 $\mu\text{g}/\text{cm}^2$, respectively. No catalyst poisoning to 100 ppm CO was observed during the power generation. Though the peak power was poor around 100 mW/cm^2 , results were satisfying for the first prototype.

1. Introduction

Fuel cells have been developed for local energy supply, because high efficiency is expected even in a small scale system and low temperature. Portable electronic devices now demand higher performance power sources and we have studied miniaturization of fuel cells with MEMS techniques. Then, we proposed fuel cells with monolithically fabricated Si electrodes as shown in figure 1¹ and promising performance more than 450 mW/cm^2 was demonstrated². However, Pt amount in the catalyst layer was 3.6 mg/cm^2 and we had to reduce the Pt usage. Besides, recent improvements of Li-ion battery are lowering expectation to miniature fuel cells. The advantage of the fuel cell, i.e. clean and efficient energy source, should be strengthened.

Biomass is one of ultimate energy sources and hydrogen can be produced by gasification of the biomass. But high CO concentration in the biomass derived hydrogen is problematic because of Pt catalyst poisoning. At PowerMEMS 2013, we reported that our Pd-Pt catalyst had promising features³. The catalyst was formed using electrochemical ALD (Atomic Layer Deposition) of Pt on porous Pd. Amount of Pt was successfully reduced to 6 $\mu\text{g}/\text{cm}^2$ and no power drop was observed during 30 minutes power generation test with hydrogen containing 100 ppm CO supply. However, the Pd-Pt catalyst uses 1.5 mg/cm^2 of Pd and reduction of Pd amount was required. Besides, the fuel cells often broke during the power generation tests. Figure 2 shows the collapses of the catalyst layer and the porous Pd collapses were supposed to be induced by repetition of hydrogen adsorption and release. Then, as shown in figure 3, we proposed the Au-Pd-Pt multilayer catalyst with porous Au core structure to suppress hydrogen adsorption and electrochemical ALD technique to fabricate Pd-Pt layered structure on an Au wire was reported at PowerMEMS 2016⁴. In this study, the electrochemical ALD was applied to porous Au layer formed on a Si substrate and construction of a fuel cell was attempted.



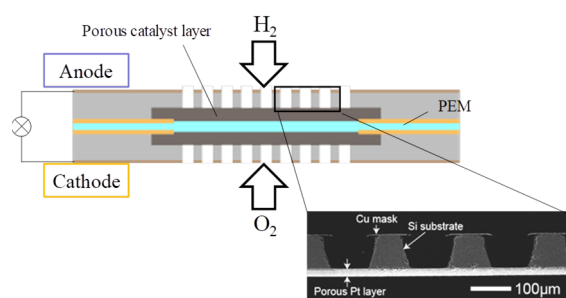


Figure 1. Miniature fuel cell with monolithically fabricated Si electrodes. Porous catalyst layer was formed on a Si substrate, and fuel channels were opened by plasma etching.

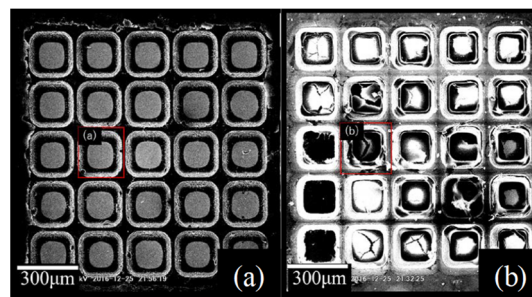


Figure 2. Top view SEM images of the Si electrodes with Pd-Pt catalyst. (a) before power generation test and (b) after the performance drop in the test.

2. Au-Pd-Pt multilayer catalyst

There is no clear evidence, but it is assumed that high CO tolerance of the Pd-Pt catalyst is realized with sub-monolayer Pt on Pd. In the previous study using Au wires, effect of Pd layer thickness on catalytic activity was investigated and it was estimated that 5 ML (Mono-layer) of Pd was required to show enough catalytic activities. Therefore, 5 ML Pd deposition on porous Au and further sub-ML Pt deposition on the porous layer was attempted.

2.1 Porous Au

Porous Au was formed using almost identical procedure reported in our previous study⁵. Porous Si was obtained by anodization in a solution containing HF. The porous Si was immersed in 20 mM NaOH solution for 300 s to remove micro porous layer on the surface and was immersed in HF solution again to remove oxide. Finally, the porous Si was immersed in Au solution for 15 minutes and porous Au was obtained by replacement reaction of Si to Au.

2.2 Electromechanical Atomic Layer Deposition(ALD)

In order to realize precise metal deposition, electrochemical ALD was employed. Figure 4 shows the schematic of the Pd deposition. Initial Pd ML can be deposited by Pd under potential deposition (UPD) and following Pd depositions are performed by H-UPD-SLRR (Surface Limited Redox Replacement)⁶. In this process, formation of a monoatomic layer of hydrogen on porous Pd is expected by under potential deposition. Then, the deposited hydrogen is replaced to Pd galvanically, and a sub-ML Pd is expected to deposit on Pd. To obtain 5 ML of Pd, 16 times iteration of this process was required in the previous study using Au wire, and identical iteration was applied to the porous layer in this study. Finally, identical H-UPD-SLRR process was applied for deposition of sub-ML Pt.

Detailed conditions of the process were listed in table 1. Mercury-mercurous sulfate electrode (MSE) was used as a reference and a Pt wire were used as a counter electrode. The Si electrode chip with the porous Au was masked by plating tapes to protect opposite side of the catalyst layer, and the Si chip was

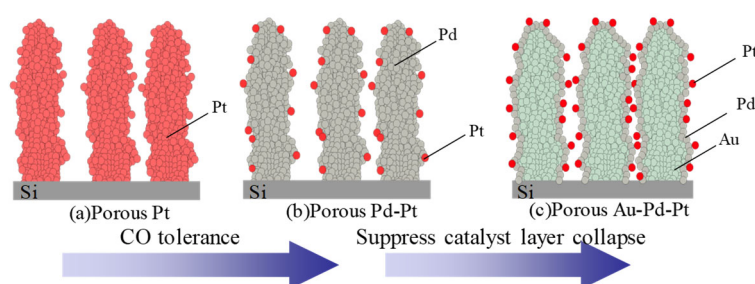


Figure 3. History of our catalyst layer structure. (a) initial Pt catalyst, (b) Pd-Pt catalyst and (c) novel Au-Pd-Pt catalyst.

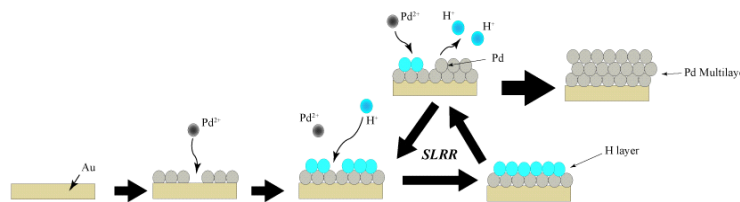


Figure 4. Schematic of the electrochemical ALD. Initially, Pd UPD is performed on Au. Then, repetition of H-UPD-SLRR is performed.

immersed in a plating solution. Initial Pd UPD on porous Au was performed by applying +80 mV (vs. MSE) for 30 minutes in a solution of 0.5 mM PdCl₂ + 1 mM HCl + 0.1 M HClO₄ and subsequent H UPD was performed by applying -600mV. Then, the electrical circuit was opened until the electrode potential reached 0mV. This process was repeated to obtain 5 ML Pd. Then the solution was switched to 0.1 mM H₂PtCl₆ + 0.1 M HClO₄ and sub-ML Pt deposition was performed.

3. Characterization of the Au-Pd-Pt catalyst layer and power generation test

Following the above described procedure, porous Au based catalyst layers were formed on Si chips and characterization of the porous layers were performed.

3.1 Elemental analysis

After the formation of the catalyst layer, specimen chip was cleaved and the cross section was observed using FE-SEM with EDS (Energy dispersive X-ray spectroscopy) (JEOL Ltd., JSM-7600F). Figure 5 shows the results of EDS analysis. Bright area in figure 5(a) is the porous catalyst layer. Strong Au signal was observed while almost no Si signal was detected in the catalyst layer. Figure 5(d) shows the Pd signal. Though slight strong Pd signal was observed at the top surface, almost uniform Pd signal was observed over the porous layer and the uniformity suggested that the electrochemical ALD worked successfully. Though Pt deposition was also performed, amount of Pt must be quite small and the characteristic X-ray spectrum of Pt is almost identical to Au spectrum. Therefore, Pt mapping was not available.

3.2 Formic acid oxidation

Electro-oxidation of formic acid is sometimes used to evaluate the CO tolerance of the fuel cell catalyst because the oxidation process involves the formation of CO before completion of oxidation to CO₂. Therefore, the Si electrode chips with the porous catalyst layer were immersed in the formic acid solution and electro-oxidation of formic acid was performed by applying constant electrode potential. Figure 6 shows the time variation of oxidation currents. Red lines are the results with the novel Au-Pd-Pt porous catalyst, while black lines are the results with our conventional porous Pt catalyst. Larger currents were observed at two different electrode potentials and higher catalytic activities were expected with the Au-Pd-Pt catalyst.

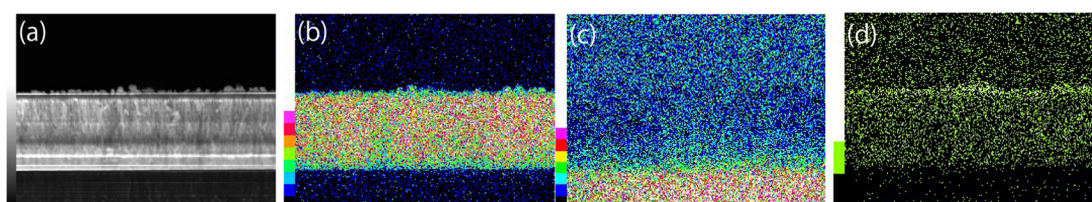


Figure 5. EDS elemental mapping of cross section of the novel Au-Pd-Pt catalyst layer. (a) SEM image, (b) Au, (c) Si and (d) Pd.

Table 1. Conditions for Pd and Pt depotition by H-UPD
SLRR on porous Au

Pd deposition	
Working electrode	Porous Au
Reference electrode	MSE
Counter electrode	Pt wire
solution	0.5mM PdCl ₂ +1mMHCl+0.1MHClO ₄
H-UPD potential [mV (vs.MSE)]	-600
H-UPD time [s]	1
SLRR potential [mV vs.MSE]	Open Circuit Potential →0
Pt deposition	
Working electrode	Porous Au-Pd
Reference electrode	MSE
Counter electrode	Pt wire
solution	0.1mM H ₂ PtCl ₆ + 0.1M HClO ₄
H-UPD potential [mV (vs.MSE)]	-600
H-UPD time [s]	1
SLRR potential [mV vs.MSE]	Open Circuit Potential →-280

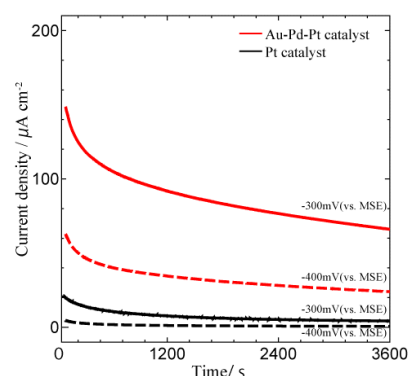


Figure 6. Oxidation current variation along time in 0.5M HCOOH + 0.1M H₂SO₄

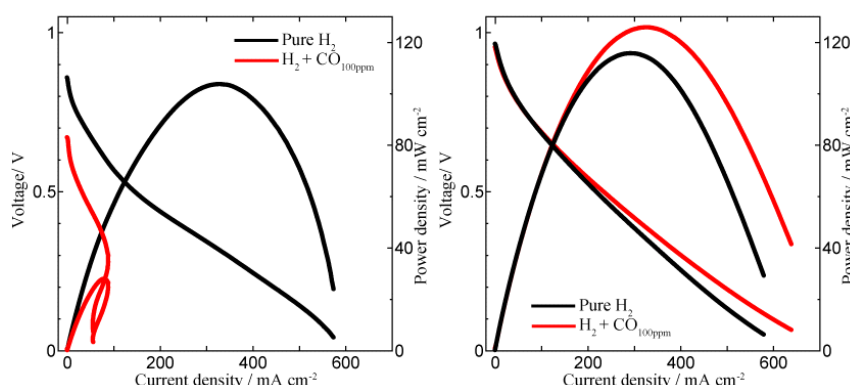


Figure 7. Polarization curves obtained with anode catalyst of (a) Pt and (b) the novel Au-Pd-Pt.

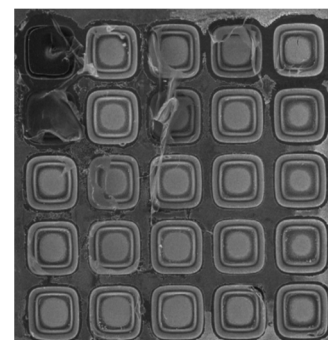


Figure 8. Top view SEM images of the Si electrodes after the power generation test.

3.3 Power generation with a prototype fuel cell

Following our conventional procedure except the formation of the novel Au-Pd-Pt catalyst layer, fabrication of the miniature fuel cells was attempted. To open the fuel channels, plasma etching was applied from opposite side of the porous catalyst layer. Compared to porous Pt, plasma etching rate of the porous Au was larger than our conventional porous Pt and plasma etching time was carefully determined to avoid damage to the catalyst layer. Finally, a prototype fuel cells was made. The fuel cell had the novel Au-Pd-Pt catalyst on one side and a conventional porous Pt catalyst on the other side. Power generation was performed at 313K with oxygen supply. Initially, pure hydrogen was supplied. Then, the gas supply was switch to hydrogen containing 100 ppm CO was supplied. Polarization curves were obtained at just before the gas switch and 30 min after the switch, respectively. During 30 min of hydrogen containing CO supply, power generation was maintained with output voltage at 600 mV. Figure 7(a) shows the results when the porous Pt was used on hydrogen side and the Au-Pd-Pt was used on oxygen side. Figure 7(b) shows the results with opposite combination when the Au-Pd-Pt was used on hydrogen side and the porous Pt was used on oxygen side. No performance drop was observed with CO in figure 7(b) and it was found that the novel Au-Pd-Pt had high CO tolerance. It was also found that relatively high output was observed when the Au-Pd-Pt was used as a cathode catalyst which needs high catalytic activity. Figure 8 shows the top view of the Si electrode with the Au-Pd-Pt catalyst layer after the power generation test. Different from the Pd-Pt catalyst, no obvious damage was observed.

4. Conclusion

In this study, Au-Pd-Pt catalyst proposed at PowerMEMS 2016 was realized on porous Au layer using electrochemical ALD. Uniform Pd signal over porous layer in EDS analysis and high oxidation currents in formic acid oxidation suggested successful formation of Au-Pd-Pt multilayer. Finally, a prototype fuel cell was fabricated and promising results for high CO tolerance and significant reduction of Pt-Pd amount were obtained. Further optimization will be performed for higher power density.

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Acknowledgement

This study was supported by JSPS Kakenhi Grant Number 17K05022.